Chemical Kinetics: Complex Reactions

Arrhenius Theory vs. Transition State Theory

Complex Reactions
- Parallel Reaction
- Serial Reactions

Kinetic Approximations
- Steady-State Approximation
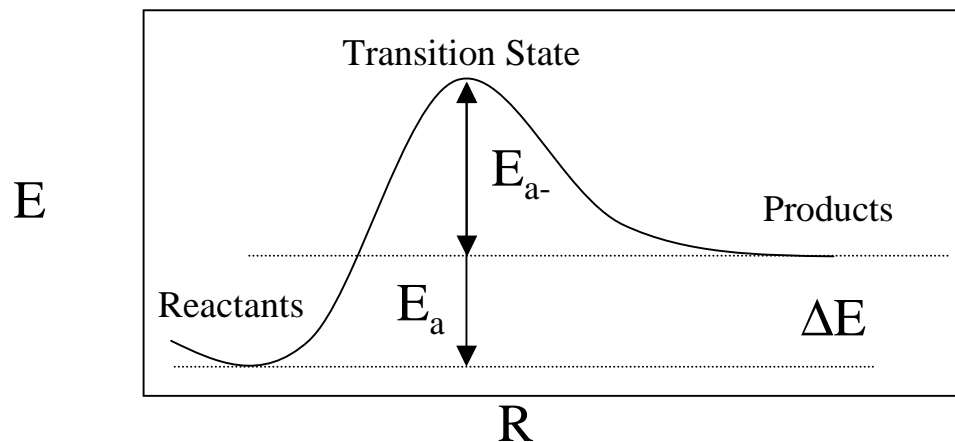- Rapid Equilibrium Approximation

- Kirchoff's Laws
- Steady-State

Last time Alex touched briefly on the Arrhenius and Transition State Theory of chemical reactions.

Arrhenius measured that for most (**but not all**) chemical reactions

$$\ln(k) = (-E_a/RT) + \ln(A)$$

$$k = A*\exp(-E_a/RT)$$

The simple explanation for this form is that there is a barrier between forming the products from the reactants:

One of the interpretations of this form is that there is a collisional term, a steric factor, and an energy term:

$$k= A*\exp(-E_a/RT)$$
$$k= Z*\sigma* \exp(-E_a/RT)$$

Because at high temperatures we are left with

$$k= Z* \sigma$$

which implies that the reactions are only collision driven

Experimentally measured rates can fall more than two orders of magnitude higher than predicted by the collision theory we derived before.
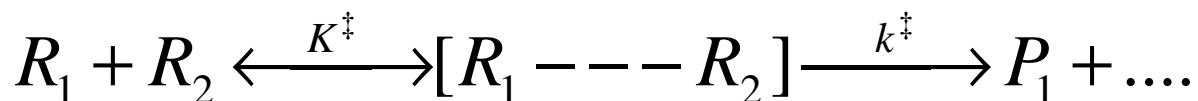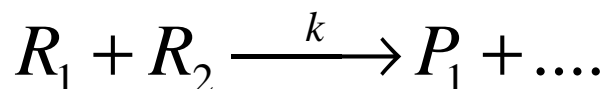
Introduction of sigma can only decrease reaction.

Also we can't explain the existence of inverse temperature dependence!

1935- Eyring and other developed transistion state theory to account for these difficulties.

As Alex mentioned the theory takes into account short lived intermediates.

$$R_1 + R_2 \xrightarrow{k} P_1 + ...$$

$$R_1 + R_2 \xleftrightarrow{K^\ddagger} [R_1 --- R_2] \xrightarrow{k^\ddagger} P_1 + ...$$

The following things are generally assumed:
1) The transition state is short lived
2) It is in low concentration
3) It is in rapid equilibrium with the reactants.

$$K^\ddagger = \frac{[R_1 --- R_2]}{[R_1][R_2]}$$

$$\dot{P} = k^\ddagger [R_1 --- R_2]$$

Now given that

$$K^{\ddagger} = \frac{[R_1 - - - R_2]}{[R_1][R_2]} = e^{-\frac{\Delta G^{\ddagger}}{RT}} = e^{-\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}} = e^{-\frac{\Delta H^{\ddagger}}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}} = \frac{k_1}{k_{-1}}$$

We find that there is both an energy and entropy barrier to overcome in forming the transition state.

Further the rate of reaction is via this theory is

$$\dot{P} = k^{\ddagger} K^{\ddagger} [R_1][R_2]$$

Now remember that

$$\Delta H = \Delta E - \Delta PV = \Delta E - \Delta nRT \quad \text{(For an ideal gas)}$$

For this process: $\Delta E \approx E_a$ and $\Delta n = -1$.

E_a is on the order of hundreds of kJ/mol.
RT is on the order of 1-2 kJ/mol

So going back to:

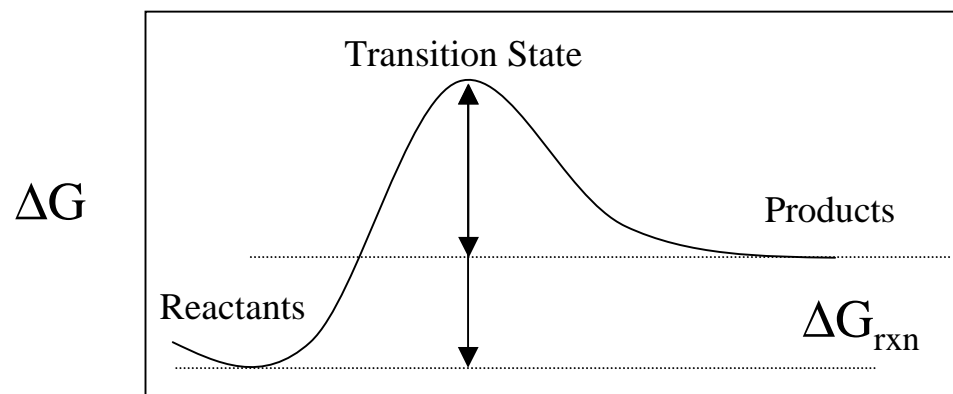$$K^{\ddagger} = \frac{[R_1 - - - R_2]}{[R_1][R_2]} = e^{-\frac{\Delta G^{\ddagger}}{RT}} \approx e^{-\frac{E_a}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}}$$

For a bimolecular, gas phase reaction. So you can see we have already a correction to the arrhenius theory going on here (sort of a stand-in for our so-called steric factor).

$$\dot{P} = k^{\ddagger} e^{-\frac{E_a}{RT}} e^{-\frac{\Delta S}{R}} [R_1][R_2]$$

So what about $k^{\ddagger}$? Well--- this is really a dissociation of the transition state into the products. There is no barrier!

We've overcome both the energy and entropy barriers and the rate of production is governed by the internal molecular motions (vibrations…) of the molecule!

From quantum mechanics we know that
$$E = h\, \nu_{vib}$$
And from classical theory:
$$E = k\, T$$
So $\qquad\qquad \nu_{vib} = kT/h = $ rate of vibration (in per seconds) $\approx k^{\ddagger}$

Thus:

$$\dot{P} = \frac{k\mathrm{T}}{h} e^{-\frac{E_a}{RT}} e^{-\frac{\Delta S}{R}} [R_1][R_2]$$

The Arrhenius form is:

$$\dot{P} = Z_{AB} \sigma e^{-\frac{E_a}{RT}}$$
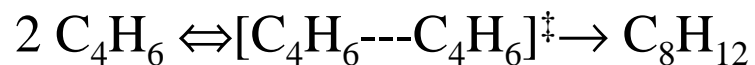
So we can identify one with the other roughly.

(Where might inverse temperature dependencies creep in?)

Examples:

Bimolecular Reactions-- Dimerization of Butadiene:

$$2\ C_4H_6 \Leftrightarrow [C_4H_6\text{---}C_4H_6]^{\ddagger} \to C_8H_{12}$$

$$\Delta S^{\ddagger} = -68\ J/K\ mol$$

For comparison a unimolecular reaction:

$$N_2O_5 \Leftrightarrow [NO\text{---}NO_2]^{\ddagger} \to NO + NO_2$$

$$\Delta S^{\ddagger} = -8\ J/K\ mol$$

Also consider protein folding:

Chymotrypsinogen at 47 °C and pH=2.0

$\Delta H^{\ddagger} = 354$ kJ

$\Delta H = 417$ kJ
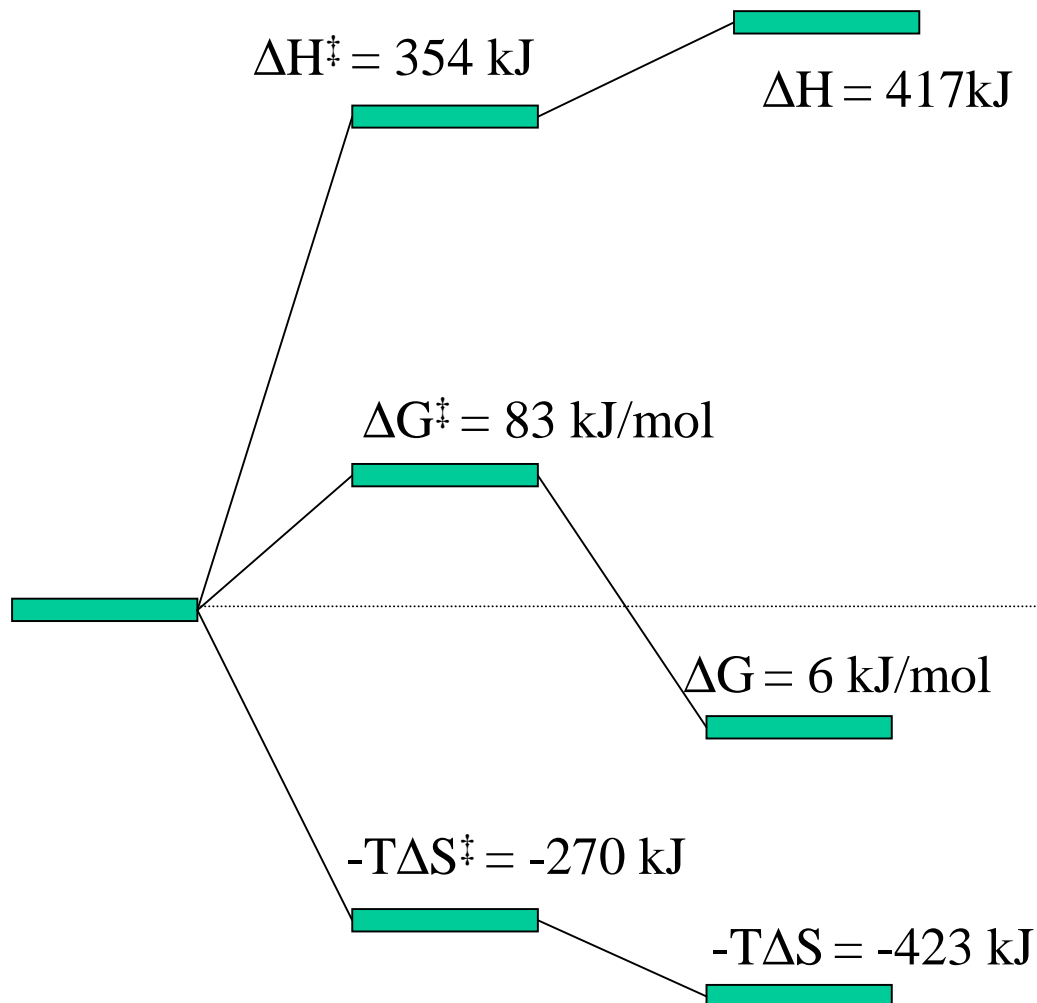
Strongly entropy driven!

$\Delta G^{\ddagger} = 83$ kJ/mol

$\Delta G = 6$ kJ/mol

$-T\Delta S^{\ddagger} = -270$ kJ

$-T\Delta S = -423$ kJ

Complex Reactions:

1) Parallel Reactions: 2) Serial Reactions

```
        B
       ↗
A
       ↘
        C
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A ———————→ B
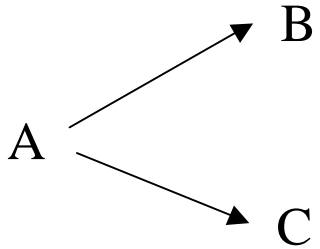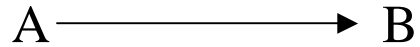
Toy system: A futile cyle.
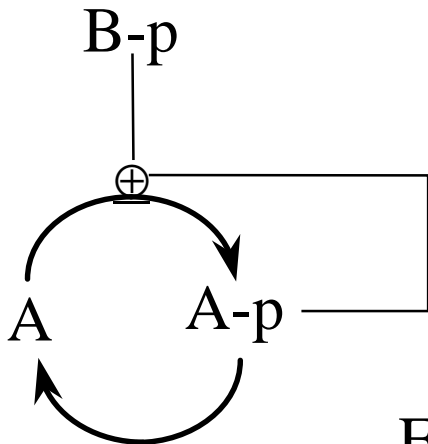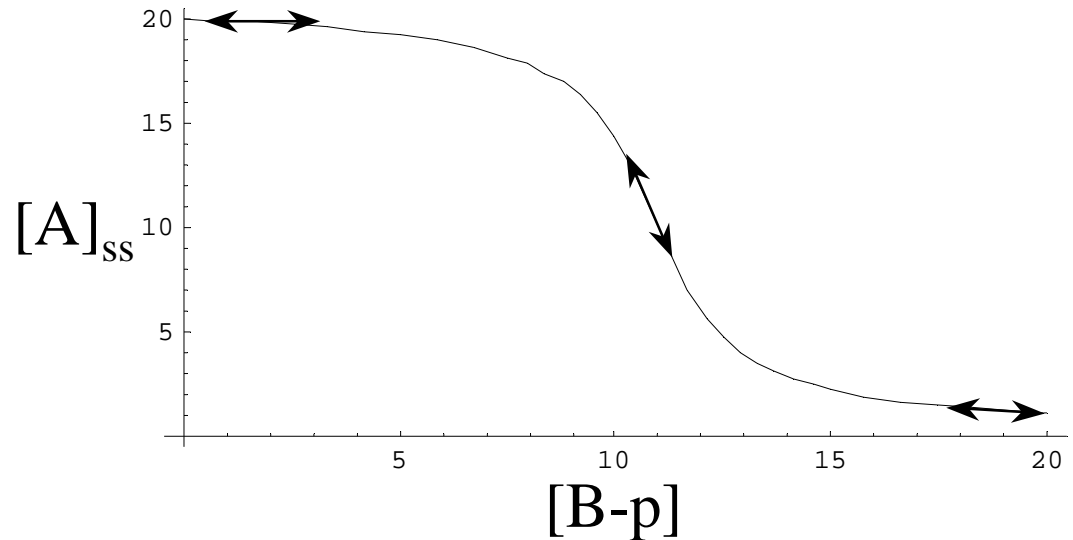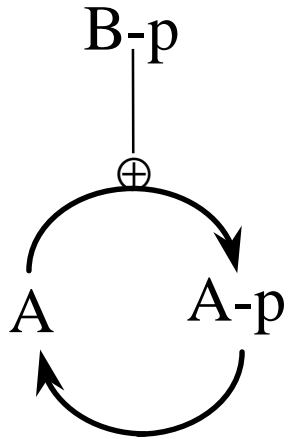
E.g. Focal Adhesion Kinase Alternative Splice

B-p
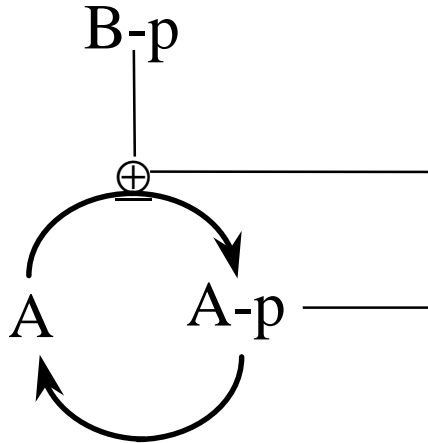
$$\frac{dA}{dt} = Dephosphorylation - (Phosphorylation_B + Phosphorylation_{A-p})$$
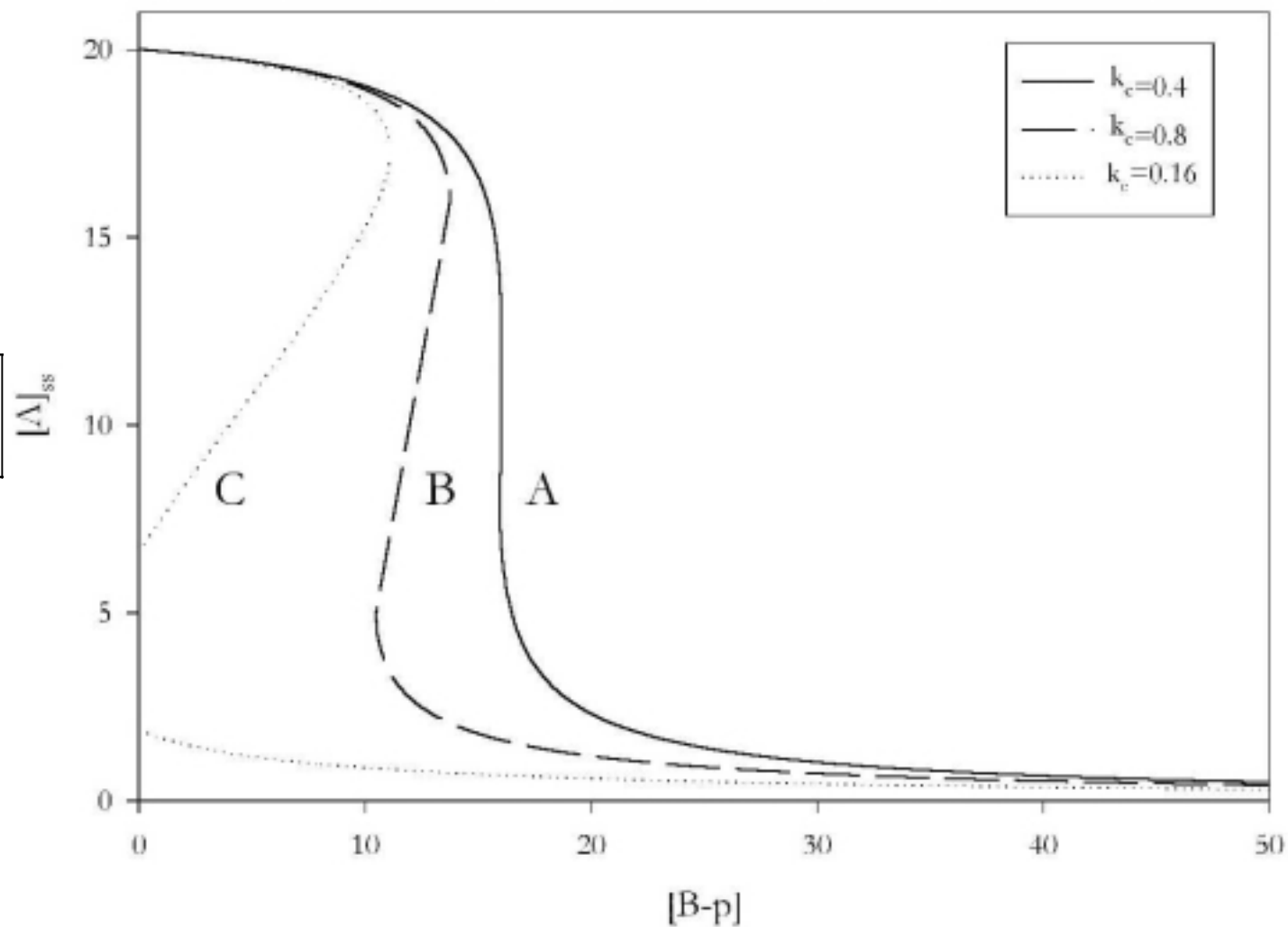
A   A-p

$$Phosphorylation_B = k_{cat-f} *[B-p]* \frac{[A]}{K_{Af} +[A]}$$
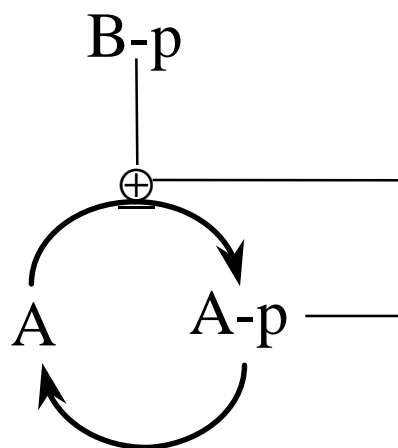
$$Dephosphorylation = V_{max-r} * \frac{[A-p]}{K_{Ar} +[A-p]}$$

$$Phosphorylation_{A-p} = k_{cat-fA} *[A-p]* \frac{[A]}{K_{Af2} +[A]}$$

Homework:

TSW

Reading: Finish Chapter 6, Chapter 7 through page 361
Chapter 6: 17,21,24,31
Chapter 7: 4,12